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PROCESSING OF ALUMINA BY-PRODUCTS IN HUNGARY

(Lecture delivered at the 1951 Annual Congress of Chemists
 by Sandor Dunay, Chemical Engineer)

The most important component of bauxite is Al_2O_3 , which constitutes 50
 to 60 percent of the ore, followed quantitatively by Fe_2O_3 , SiO_2 , and TiO_2 .

Analysis of bauxite mined at Gant yielded the following data:

Content	Percent	
	From	To
Al_2O_3	55	57
SiO_2	3	4
TiO_2	2	3
Fe_2O_3	17	20
CaO	0.2	0.3
MgO	0.05	0.15
MnO_2	0.3	0.8
Cr_2O_3	0.03	0.08
V_2O_5	0.04	0.1
P_2O_5	0.3	0.5

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<u>Content</u>	<u>Percent</u>	
	<u>From</u>	<u>To</u>
ZrO ₂	0.05	0.09
BeO	0.005	0.012
ZnO	0.004	0.007
NiO	--	0.001
As ₂ O ₃	--	0.002
SO ₃	0.01	0.02
S	0.00	0.01
CO ₂	0.1	0.2
C	0.2	0.5
H ₂ O	14	19

The F content of Hungarian bauxite is in general about 0.1 percent.

The compounds which form bauxite may be divided into three groups according to the Bayer process. The first group is formed of substances which contain nitrate salts soluble in caustic soda solution; the second group consists of substances which are not soluble in the solution; and the third group is soluble at the time of extraction, but becomes insoluble when diluted.

Quantitatively the most important by-product is red mud. The liquid portion of red mud separated by Kelly filters is about 50 percent. It is not possible to wash the sodium aluminate out from the red mud completely, because when the electrolyte is removed it turns into an unfilterable colloid. For this reason red mud always retains the components of the aluminate solution, although in tiny quantities.

The composition of red mud varies by bauxite and by factory. The following composition is typical:

<u>Content</u>	<u>Percent</u>	
	<u>From</u>	<u>To</u>
SiO ₂	6	9
TiO ₂	3	7
FeO	40	55
Al ₂ O ₃ [sic]	16	22
CaO	--	1
MgO	--	0.5

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Content	Percent	
	From	To
Total Na_2O	7	10
H_2O	6	8
Miscellaneous	1	2

Red mud is composed substantially of compounds that are not soluble in caustic soda solution. If we concentrate on the most vulnerable aspect of the Bayer method, that is, the loss of sodium, then we must examine in detail the sodium compounds which, forming at the time of extraction, remain insoluble in aqueous sodium hydroxide.

According to the literature, at the time of extraction or at the time of settling, two compounds are formed which cause loss of soda: natrolite (sodium aluminum hydrosilicate) and sodium metatitanate.

The formation of natrolite is connected with the SiO_2 content of bauxite and causes loss of both sodium oxide and aluminum oxide. According to Belyayev (1), each percent of SiO_2 per ton of bauxite causes 6.5 kilograms of NaOH and 8.5 kilograms of Al_2O_3 to pass into the red mud.

To make these figures more clear, assume that 250,000 tons of bauxite are used annually to obtain 100,000 tons of alumina. If the SiO_2 content of the bauxite averages 3 percent, then according to Belyayev's data about 6,300 tons of Al_2O_3 and 3,000 tons of NaOH pass into the red mud every year.

The findings for the composition of natrolite vary, due presumably to the fact that we do not get natrolite of the same composition from different bauxite ores and by different technological processes. The same bauxite and the same process yield a sodium aluminate liquor with a constant SiO_2 content.

The behavior of dissolved silica in aluminate liquor has been investigated by the Soviet scientist M. G. Leiteisen. (2) According to his findings, a dissolved SiO_2 concentration belongs to every sodium aluminate concentration. When he increased the quantity of the dissolved SiO_2 he obtained natrolite until the aluminate-silica relationship became balanced. The constant value of the balance at a temperature of 70 degrees centigrade was, he found, 2,000 to 2,100 if he measured the concentration in grams per liter. If the free Na_2O content in the aluminate solution was high, then the balance showed a variation from the above value, because the solubility of SiO_2 was greatly increased. We can clearly see the danger of economic loss resulting from the Bayer process in the silica content of bauxite.

The other component of bauxite which decreases the soda content is TiO_2 , which is present in the form of anatase. (3)

According to Belyayev, TiO_2 passes into the red mud in the form of $\text{Na}_2\text{O} \cdot 2\text{TiO}_2 \cdot \text{H}_2\text{O}$ and each percent of TiO_2 content in a ton of bauxite causes a loss of 5.04 kilograms of NaOH. In bauxite containing an average of 2.5 percent TiO_2 there is a loss of 3,150 tons of NaOH processing 100,000 tons of alumina.

In the course of our investigation of red mud it became possible to isolate a new compound. In one of our alumina plants we were able, by using a 0.2-millimeter sifter, to separate about 5 percent dust matter from the total dry substance, despite the fact that the bauxite had been ground to flour fineness before extraction. We washed thoroughly the part that had been separated and

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dried it at 105 degrees centigrade. We saw that the greater part of the substance was red-colored grit mixed with alumina-hydrate flakes. To separate the two substances we reduced the iron by the use of illuminating gas at a temperature of 450 to 500 degrees centigrade and made it magnetic, a quality which it retained even after reoxidation at a temperature of 400 to 500 degrees centigrade. The part isolated by magnetism had the following composition:

$$5 \text{ Fe}_2\text{O}_3 \cdot 1 \text{ TiO}_2 \cdot 1 \text{ Al}_2\text{O}_3$$

Over a period of time we examined additional samples from this factory and established a constant composition for the dust, which we named Dorr dust. The Dorr dust which we obtained in a similar manner from the red mud of another alumina factory yielded by analysis the following composition: $8 \text{ Fe}_2\text{O}_3 \cdot 1 \text{ TiO}_2 \cdot 1 \text{ SiO}_2$

It is noteworthy that aside from a tiny amount of impurity, we found no Na_2O in the Dorr dust, which throws doubt on the theory that the TiO_2 content of bauxite passes into the red mud in the form of Na_2TiO_3 or NaTiO_3 or $2 \text{ Na}_2\text{O} \cdot 5 \text{ TiO}_2 \cdot 5 \text{ H}_2\text{O}$. According to this theory the loss of sodium due to the TiO_2 content of bauxite is but partly valid.

On the basis of what has been said we may indicate the composition of red mud as follows: Red mud contains the substances that did not dissolve in the caustic soda solution, including the Al_2O_3 which remained undissolved, natrolite, sodium hydrometallite, the compounds that form Dorr dust, and a tiny amount of sodium aluminate liquor, together with its impurities.

If we examine the substances in red mud from the viewpoint of their economic value, then we find that its TiO_2 , Al_2O_3 , and Na_2O content is very important; in addition, the good-quality raw iron which may be obtained from the red mud should not be neglected, especially in countries deficient in iron ore. Finally, the chromium, vanadium, and rare metal content of red mud are valuable if they can be extracted economically.

We came to the surprising result that the value of the substances in red mud approaches, or perhaps even exceeds, the value of the alumina to which the red mud belongs. This finding is valid for all bauxites which can be extracted economically by the Bayer process. In the case of low-grade bauxites the advantage increases.

At the congress of the Hungarian National Mining and Metallurgical Association, held 9 - 11 December 1949, Dr Bela Lanyi gave a detailed account of the processes suggested for the use of red mud. (4)

If we examine the value of the compounds that form red mud, TiO_2 is first, followed by Al_2O_3 , Na_2O , and finally Fe_2O_3 . To illustrate the values, let us place the value of TiO_2 at 100; in that case Al_2O_3 is 35 and Na_2O is 23. On the other hand, the iron that may be obtained from Fe_2O_3 is of very small value. Clearly, the primary aim of the investigations was to obtain titanium compounds.

Without attempting to be complete, let us examine several types of methods suggested for processing red mud.

The greater part (50 to 60 percent) of the Na_2O content of red mud can be separated by the methods based on H. C. Peffer's patent (5), which replace the Na_2O of red mud by CaO . The disadvantage of this process is that the Al_2O_3 contained in the red mud is lost and the CaO contents of this so-called "limed" red mud rises to about 20 percent.

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In Hungary, increasing use of limed red mud can be expected until a newer, more modern method can be found. Our metallurgists, in any event, can count for a long time only on limed red mud.

Recovery of Na_2O and Al_2O_3 is the aim of those processes by which the red mud is shrunk or dissolved through the use of anhydrous soda. About 75 percent of the Al_2O_3 content is obtained in the form of NaAlO_2 . By this process a great deal of silica gets into the solution and must be separated subsequently. The secondary red mud which is obtained resembles the red mud obtained by the pyrogenic method; consequently, it can bind hydrogen disulfide, that is, it can be used as a gas-purifying agent. Besides, due to its high iron oxide content, it is good metallurgical raw material and TiO_2 can be obtained from the slag that forms at the time of its refinement into iron.

A large number of investigators have dealt with the problem of removing silica from the sodium aluminate liquor. According to the methods of Muller, Yakovkin, and Penyakov (6), the aluminate liquor is freed from its SiO_2 content in an autoclave.

G. V. Labutin and S. G. Koltypin (7) also perform the process in autoclaves at 150-155 degrees under a pressure of 3.5 to 3.7 atmospheres.

According to Pelyayev (8), the silica can be removed from the aluminate liquor by steady heating, or by boiling with lime water in slightly concentrated solutions, when $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2 \text{SiO}_2 \cdot 2 \text{H}_2\text{O}$ is formed.

M. M. Loboda (9) adds lime to the aluminate solution and removes the silica in an autoclave at 150 degrees centigrade. A. P. Snoiko (10) treats the aluminate solution with lime salts at low pressure at 95 to 101 degrees centigrade to cause precipitation of the silica.

According to the patent of Znoikov (11), the red mud is steeped in caustic soda solution with Na_2CO_3 and CaO and the filtrate is cleared of silica with CaO .

Methods for obtaining TiO_2 may be divided into five groups:

1. The red mud is dissolved and the salts are produced in different forms. From the resulting salt solution metatitanic acid is obtained by hydrolysis. (12) The dissolution of red mud can be carried out so that the iron and titanium compounds remain. (13)
2. The red mud is reduced and the spongy iron obtained is separated by dilute acids or iron chloride, leaving a titanium-rich substance. (14)
3. The iron is extracted from the red mud and the titanium-rich slag is processed into titanium dioxide. (15)
4. The properly prepared red mud is chlorinated under reduction, e.g., by sulfidizing, and the titanium is separated in the form of TiCl_4 . (16)
5. By treating the red mud with sulfur dioxide the bulk of the iron is separated; by this process the TiO_2 content of the residue is increased. (17)

These proposals (with the exception of 4) aim at the increase of the TiO_2 content; the subsequent extraction of TiO_2 takes place generally with sulfuric acid.

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The processing of red mud is included in the program of the Metal Research Institute. Successful solution of this problem would lower the cost of alumina and enable us to obtain materials which up to now have had to be imported.

It was clear to us that the problem of processing red mud had to be solved by the gradual extraction of the component parts without the aid of diluting compounds. The results of our investigations are as follows:

Breaking up the natrolite content of red mud by thermic treatment and using a dilute lye, 50 to 60 percent of the Na_2O and Al_2O_3 content is separated.

If unwashable red mud is processed, then the temperature used in the thermic treatment is much lower. In this case part of the SiO_2 remains in the extracting solution in a dissolved state, and consequently it is necessary to take steps to remove it. This can be done by use of the processes already described for the removal of silica.

By our method -- especially in the processing of fresh mud -- a secondary red mud is obtained which has an iron content of 65 to 70 percent; its TiO_2 content ranges up to 10 percent.

If the secondary red mud (which may now be regarded as titanium-bearing iron ore) is refined into iron, we obtain in addition to high-quality iron a slag with a TiO_2 content of between 20 and 22 percent. When slag-forming materials are used in the slag, the TiO_2 content increases to 14-16 percent.

The further processing of our titanium-rich slag takes place with sulfuric acid, and from the solution metatitanic acid and ultimately TiO_2 can be produced.

Our method is now being applied in medium-sized plants. As long as our laboratory results are not tested under operational conditions and the production of enriched red mud is not undertaken on a large scale, our metallurgists can count only on limed red mud.

From the liquor, thickened by heating, salts are obtained which are called vanadium mud, phosphate mud, sulfate mud, and lixivial salts.

The analysis of dry vanadium mud yielded the following data:

Content	Percent	
	From	To
Al_2O_3	1.5	6.5
SiO_2	0.01	0.08
Fe_2O_3	0.02	0.90
V_2O_5	0.3	7.3
P_2O_5	0.75	8.75
As_2O_3	0.03	0.8
Cl	0.1	0.4
SO_4	8.0	20.0

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Content	Percent	
	From	To
CO ₃	10.0	15.0
Na ₂ O	50.0	55.0
C	0.3	0.5
F	4.0	6.5
H ₂ O removable at 600 degrees centigrade	2.5	3.0

Hungarian scientists have dealt successfully with the problems of processing vanadium mud. (18, 19) The methods are based on two principles.

According to one principle the vanadium compounds are separated from the water solution in a form that does not readily dissolve, and this enriched substance is processed. By the other principle, the enriched substance and subsequently vanadium compounds are obtained by separating other compounds from the vanadium mud.

The method used by the Metal Research Institute, as is the case of red mud, is based on gradual separation.

First we remove from the water solution all substances, first of all Al₂O₃ and P₂O₅, which would reduce the pureness of the vanadium that is obtained as a final product. These are removed by saturation with carbonic acid. The precipitate contains Al₂O₃ bound in part to P₂O₅ and in part in the form of a complex fluoride. The fluoride content of the precipitate is about 15 percent. If the vanadium mud contains a greater amount of P₂O₅, the separation in the form of aluminum phosphate is effected by adding aluminate caustic soda solution.

The solution filtered from the precipitate that resulted from the carbonic acid is distilled and its sodium sulfate mixture is crystallized. The mixture of salts obtained in this manner is used in glass factories. From the mother liquor filtrated from the sodium sulfate we separate ammonium metavanadate by the addition of ammonium chloride. The liquor goes back into use, and hence there is no loss of vanadium at any point. Our method can be carried out in ordinary iron equipment. The ammonium metavanadate can be transformed into V₂O₅ which can be used in the production of ferrovanadium and for chemical purposes. (19)

The vanadium-bearing sodium-fluo-phospho-vanadate is easily soluble in hot water (but not in cold) and in caustic soda solution. Therefore, in the course of the alumina production it may separate at every phase where the caustic soda solution cools.

In the Dorr vessels the aluminate liquor is still boiling and separation does not take place. In the mixing vessels the aluminate liquor cools to a considerable degree and the crystals of the vanadium compound appear as deposits. The deposits removed from the sides of the mixing vessel contain, in addition to 70 percent of aluminum hydroxide, 30 percent of water soluble crystals, which are for the most part a mixture of vanadium compounds, sodium sulfate, and soda.

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The processing of these deposits is done most expediently by removing the water soluble parts with boiling hot water, the solution being processed like vanadium mud; the solid parts, which are almost pure aluminum hydroxide, are returned to alumina production.

In the pipes and on the walls of the hydroseparator used for precipitating the aluminum hydroxide we found large, octahedral crystals which we named hydroseparator crystals. They consist of sodium-fluo-phospho-vanadate. They are processed like vanadium mud.

In time, hard deposits form on the sides of the Dorr vessels. These are named Dorr slate. Its main bulk is crystalline sodium aluminum hydrosilicate with red mud impurities. Mixed with red mud, it can be processed. The quantity of Dorr slate is insignificant.

BIBLIOGRAPHY

1. Belyayev, Kennyufemek kohaszata (Metallurgy of Light Metals).
2. Leitesen, M. G., Legkiye Metally (Light Metals). Vol V, No 10, 1946, pp 34-40.
3. Kutas, A., "Timfoldgyartas" (Alumina Production), Aluminium (Aluminum).
4. Lanyi, B., Dr., "A Bayer eljaras vorosiszapjanak hasznositasa" (Utilization of Red Mud in the Bayer Process), Panyaszati es Kohaszati Lapok (Mining and Metallurgical Journal).
5. Peffer, H. C., US Patent 936, 270, 1909.
6. Muller, Yakovkin, Penyakov, German Patents 80,063 and 93,925.
7. Labutin, G. V., and Koltypin, S. G., Legkiye Metally, Vol 5, No 11, 1936, pp 7-13.
8. Belyayev, Kennyufemek kohaszata, p 103.
9. Loboda, M. M., Legkiye Metally, Vol 5, No 1, pp 5-10, 1936.
10. Snicko, A. F., Soviet Patent 48,275, 1936.
11. Znoikov, Soviet Patent 46,561, 1936.
12. Hunyadi, German Patent 665,236, 1937.
13. Vereinigte Aluminium Werke (United Aluminum Works), German Patent 702,397, 1941.
14. Vereinigte Aluminium Werke, German Patent 525,908, 1927.
15. Montecatini, Italian Patent 381,980, 1940.
16. Makray, Hungarian Patent 115,530, 1933.
17. Metallgesellschaft A. G. (Metal Company, Inc.), German Patent 478,740, 1928.
18. Veres, Imre, "A hazai vanadiumszapok feldolgozasanak nehany kerdesere" (Several Problems Concerning the Processing of Domestic Vanadium Mud), Magy. Kem. Folyoirat (Hungarian Chemical Journal), Aug 1951.
19. Vajk, Peter, "A vanadium kohaszata es felhasznalasa" (The Metallurgy and Utilization of Vanadium), Kohaszati Lapok (Metallurgical Journal), No 1, 1951.

COMMENTS

- A. Comment by Mrs Andras Nagy, Ph. D.

The lecturer's investigations and findings concerning Dorr dust are interesting. However, the analysis of Dorr dust before reduction is lacking, as is a detailed analysis of Dorr dust after magnetization.

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The lecturer assumes the formation of a new soda-free compound. My own thoughts -- based on the findings of Lyubimov, a Stalin-Prize-winning geologist -- are different. According to Lyubimov, iron was found in boehmite or hydrargillite crystals. This was established through many experiments, because in the dissolution of bauxite with hydrochloric acid this iron cannot be separated without destroying the entire structure of the lattice. The presence of this iron in the crystals is characteristic of certain bauxite types.

One can assume a similar phenomenon in the formation of Dorr dust, with the difference that, in the crystals of the iron compound, alumina is formed which is not dissolved at the time of extraction, i.e., always has the same constituents. That is why the same bauxite and the same technological methods of production always yield dust with identical content.

It would be interesting to know the iron content of Dorr dust prior to reduction. Our laboratory has carried out experiments on the iron content in bauxite mined at Isaka and found it to be 0.23 percent FeO. It is possible that the iron content has considerable influence on the fact that the composition of Dorr dust varies.

In 1946, Dr. Kornyei was studying in our laboratories the speed of sedimentation of red mud from different kinds of bauxite. It was found that after extraction conducted in a reducing atmosphere the red mud settled almost as well as with the use of hardening substances. In the light of Dunay's experiments, I should consider it very interesting to know the detailed composition of reduced red mud in connection with the formation of Dorr dust.

Some time ago, we conducted experiments in our laboratories on the use of Payer red mud as a gas-purifying agent. According to our experiments, absorbing capacity was greatly increased by the addition of 3 to 5 percent NaCl to the mixture before condensation by sodium.

In connection with the processing of red mud, the exploitation of its chrome content, of which the lecturer did not speak, may also be mentioned. On an average there is 0.07 percent of chromium oxide in bauxite which after extraction increases to about 0.2 percent in the red mud. It would be a significant gain for our national economy if our research institutes were to solve the problem of obtaining this chromium for our industry.

The experiments in connection with the traces of rare and radioactive elements found in bauxite are also interesting. When bauxite is processed, these elements (hafnium and gallium) must become enriched. Where can they be found? According to Soviet scientists, gallium is soluble in caustic soda solution as $Ga(OH)_3$ and forms deposits on the pipes beside aluminum hydroxide.

The salvaging of the valuable substances of vanadium mud can be regarded, as Dunay said, as one of our solved problems. Besides the successful experiments of the Metal Research Institute, other institute and factory laboratories have successfully completed such experiments. We can say that there are now five methods for processing vanadium mud, each of which can be used industrially.

I should like to relate briefly the principles of the Maszobal (Magyar-Szovjet Bauxit Rt., Hungarian-Soviet Bauxite Corporation) laboratory method. It was our principle to work with the richest materials in vanadium mud and consequently to enrich the poorer vanadium muds. We succeeded and obtained crystals which had a V_2O_5 content of approximately 10 percent. Only one percent of the vanadium remained in the mother liquor which could be used several times again, and the other substances (sodium carbonate, sodium sulfate, etc.) were separated thereafter.

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The advantage of our method, as well as that of the Metal Research Institute, is that we can employ leaching, i.e., iron equipment. In contrast to the lime methods, we do not get a lime mass which is difficult to filter, and in contrast to the acid methods, strong formation of bubbles, which is always undesirable in a plant, is avoided.

B. Comment by Peter Vajk

At the meeting of the Hungarian Academy of Sciences last year, Gyorgy Osztrovski pointed out the importance of extracting the hidden substances from domestic raw materials. The Hungarian Academy of Sciences, recognizing the importance of this endeavor, set up a number of subcommittees to solve the problems of bauxite processing. It placed a great deal of emphasis on the by-products of alumina production, particularly on the extraction of titanium and vanadium. The committee which dealt with this problem evaluated the various scientific results from the viewpoint of economy. An exceptionally interesting method was worked out by Imre Veres, and special mention should be given to the Barta-Kutar-Tetetleni method. The value of the latter method is that it was worked out and introduced in a very short period of time. As a result, we have been producing vanadium oxide for several months now in Hungary.

C. Comment by Dr Istvan Balint

It is well that the Metal Research Institute is conducting research on the processing of red mud in the fields most significant to our economy -- the salvaging of sodium and aluminum hydroxides.

The process which has been suggested by the Metal Research Institute has the advantage over the one now being used in one of our alumina plants that not only the sodium hydroxide but also 50-60 percent of the aluminum hydroxide can be reclaimed.

The formation of Borr dust is good news, because it shows that the harmful capacity of titanium dioxide to reduce the sodium hydroxide concentration is not as great as indicated in foreign scientific literature.

It is worth mentioning that I noticed a phenomenon similar to that of the formation of Borr dust during the conduct of experiments with vanadium salts mined at Ajka. A certain percentage of the insoluble parts of vanadium salts, dried at 100 degrees centigrade and ground to flour fineness, gathers at the time of dissolution in water and forms small pebble-like particles. This substance does not contain vanadium nor, according to my experiments, sodium.

The lecturer gives two groups of methods for processing vanadium salts: those which separate the vanadium, and those which separate mostly the accompanying substances.

In the first group he does not differentiate between the methods which separate vanadium or vanadate in a neutral, acid, or caustic soda solution. In foreign patent literature we are familiar with many methods for the use of acid, neutral, or 8 pH solutions. However, Hungarian scientists -- myself the first -- laid the foundation of the production of vanadate from sodium hydroxide liquor.

I saw possibilities in two compounds for separating vanadium as vanadate in caustic soda solutions above a pH of 10. One was calcium vanadate and the other lead vanadate. Calcium vanadates are soluble or insoluble. Metavanadate dissolves well, orthovanadate not so well. I found that a vanadate with the formula $5 \text{ CaO} \cdot \text{V}_2\text{O}_5$ dissolves least readily.

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By the production of sodium vanadate with the soda solution and the introduction of carbonic acid the production is complete, but the solution contains some sodium phosphate.

My own findings are not known in foreign literature, namely:

The separation of calcium vanadate by lye solutions takes a long time, even when the solutions are heated to the boiling point.

The vanadium content of the precipitate which contains basic calcium vanadate can be dissolved by the introduction of carbonic acid.

The vanadium content of the precipitate can be dissolved by sulfuric acid. By the admixture of calcium carbonate, all impurities can be separated from this solution, while the calcium vanadate remains in the solution.

The calcium vanadate produced by the introduction of carbonic acid contains practically no impurities, but the extraction of the vanadate is poor.

Extraction is complete in the case of sodium vanadate produced by soda solution and the introduction of carbonic acid; however, the solution also contains a small amount of sodium phosphate.

The calcium vanadate obtained by the neutralization of the sulfuric acid-vanadium solution is pure, but impurities that may be present (particularly aluminum) precipitate part of the vanadium and spoil the yield. The pure calcium vanadate is apparently adequate for metallurgical material, or various vanadium compounds can be produced from it.

On the basis of the above observations I recommend the following method for processing vanadium salts if we wish to get a caustic soda solution as a by-product:

We dissolve the vanadium salts in as much water as is needed so that after adding alkali we achieve the desired concentration of caustic soda solution. With this we mix an equal amount of caustic soda solution formed by preceding addition of alkali. After cooling we mix it with lime water for about one hour. The calcium vanadate does not separate with the mixing, but the aluminum does so entirely, and the greater part of the phosphate also does not so in the form of calcium salts. Thereafter, the material is subjected to boiling alkali for a fairly long time, the calcium vanadate separates and a caustic soda solution of equal concentration is formed. Half of this is placed into a new portion of vanadium salts, and so on. The calcium vanadate that separates also contains calcium carbonate and calcium phosphate. From this we can obtain absolutely pure calcium vanadate in the form of calcium metavanadate solution by dissolving with sulfuric acid and neutralizing with calcium carbonate.

In connection with my further research on vanadates I made the hitherto unknown observation that lead vanadate within certain pH limits is practically insoluble, while the vanadium-lead salts are soluble. This finding gives a means for much better separation of vanadium than the calcium vanadate method.

The further processing of lead vanadate may vary, depending on what kind of vanadium compound we desire and what means we choose for the regeneration of the lead compounds used in the separation. For the separation of vanadium from the solution and the regeneration of lead compounds I offer the following method:

We add lead sulfate to the vanadium salt solution and after about one hour's heating and mixing we filter the lead vanadate from the rest of the solution. We dissolve the lead vanadate in about 15 percent cold nitric acid. With sulfuric acid we convert the lead nitrate in the solution into insoluble lead sulfate, which we separate by filtration.

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The nitric acid, or to be more precise the vanadium pentoxide, separates after distillation in crystal form. After complete boiling down or filtration the vanadium pentoxide can be isolated.

The vanadium can be separated by lead vanadate from more condensed solutions. If we want to obtain a caustic soda solution from the remaining solution, then about a 10-percent caustic soda solution is obtainable instead of the 4-percent solution obtained by the calcium vanadate method. The lead vanadate method is especially useful if we want to use other vanadium salts for the production of trisalts.

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